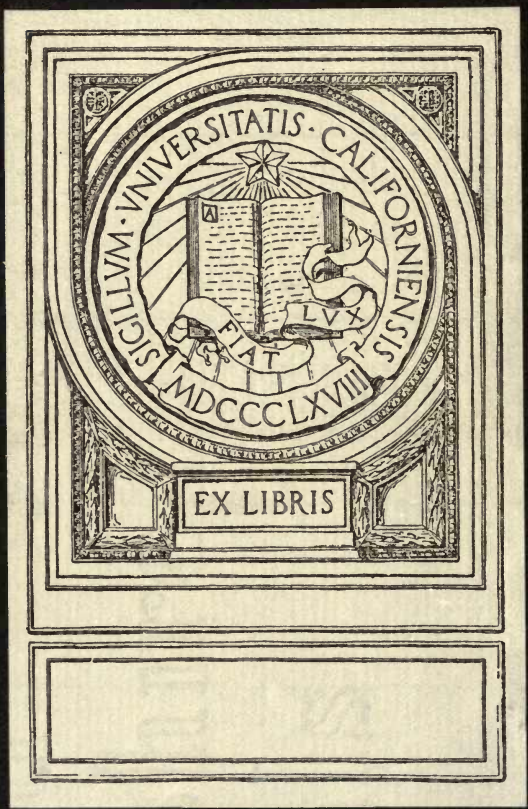
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MEASUREMENT OF MERCURY VAPOR PRESSURE BY MEANS OF THE KNUDSEN PRESSURE GAUGE

BY

CHARLES FRANCIS HILL

A.B. University of Illinois, 1914
A.M. University of Illinois, 1916

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN PHYSICS IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1921.

URBANA, ILLINOIS
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MEASUREMENT OF MERCURY VAPOR PRESSURE BY MEANS OF THE KNUDSEN PRESSURE GAUGE.

BY CHARLES F. HILL.

SYNOPSIS.

Vapor Pressure of Mercury, 0 to 35° C.—The disagreement among the results obtained by previous observers for this range of temperature suggested the need for a *direct determination* of the vapor pressures *with a Knudsen gauge.* Impurities were eliminated by numerous distillations in a system cut off from the pump by a liquid air trap, and the slight amount of residual gas was corrected for. The readings obtained at 19 temperatures lie near a smooth curve which, it is believed, gives the vapor pressures to within 3 per cent. The values for 0, 10, 20, and 30° C. are, respectively, .000350, .000775, .00182 and .00407 mm. of Hg, considerably higher than those obtained by Knudsen in 1909, but agreeing fairly well with Morley's results up to 15°, and at higher temperatures with values extrapolated from the results of Ramsey and Young.

HISTORICAL.

WHILE engaged in experimental work in the spring of 1920, an accurate knowledge of the vapor pressure of mercury at room temperature became of importance. On looking for the values given in tables for temperatures below 40° C. very little agreement among the various observers was found as may be seen in the following table.

TABLE I.

T.	Regnault 1862.	Hagen 1882.	Hertz 1882.	Ramsey and Young 1886.	Van der Plaats 1886.	Morley 1904.	Knudsen 1909.
0°	.02	.015	.00019	——	.00047	.0004	.000184
10°	.0268	.018	.0005	——	.0008	.0008	.0005
20°	.0372	.021	.0013	——	.0013	.0015	.00188
30°	.053	.026	.0029	——	——	.003	.00278
40°	.0767	.033	.0063	.008	——	.006	.006
50°	.112	.042	.013	.015	——	.011	.0126
60°	——	——	——	——	——	.021	——
70°	——	——	——	——	——	.04	——

In 1886 van der Plaats[1] published results obtained by taking a large number of readings between 0 and 20° Centigrade. Values from his mean curve are usually given preference in tables. The method was to pass dry gas through water, through sulphuric acid, and then through mercury until saturated, after which the mercury was collected by gold and pumice stone and weighed. The vapor pressure was calculated from the data obtained by comparison with the vapor pressure of water.

[1] Rec. Trans. Chim., 5, p. 49, 1886.

Van der Plaats' readings show considerable variation, but are consistent enough so that with the number of readings taken his results must be given considerable weight. The method would not be expected to give values too high since his chief error should be loss of evaporated mercury.

E. W. Morley[1] in 1904 used practically the same method as van der Plaats except that the evaporated mercury was measured by weighing the sample before and after evaporation. Readings were taken at 16, 30, 40, 50, 60 and 70° C., and Dalton's equation

$$P = ab^t$$

was used for the calculation of the mean curve and for extrapolation to 0° C. Morley's readings at 40, 30 and 16° C., are from 8 to 20 per cent. below his mean curve but at the higher temperatures his values agree with those given by others. Vapor-pressure curves should have a decreasing per cent. increase as the temperature increases. Morley's curve is perfectly uniform if the slope is measured in this way, but the error in the readings at low temperatures could easily account for this fact. While Morley can not claim a high percentage accuracy his agreement with van der Plaats at low temperatures, and with the other observers at higher temperatures, seems to indicate that the order of his values is correct.

The last data of importance published were those of Knudsen[2] in 1909. An equation was developed for the flow of gas through a tube with a small opening over one end, and an apparatus based on this equation was arranged so that the vapor pressure of mercury could be measured. This equation

$$G = \sqrt{\frac{p' - p''}{W' + W''}} \times t$$

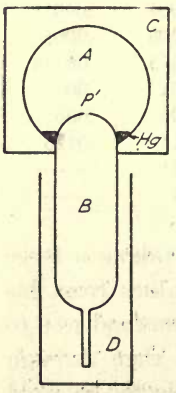

Fig. 1.

involves the pressure difference, the resistance of tube and opening, the density of the gas and the time. G is the mass of the gas or vapor which will flow through the small opening in an evacuated tube, as shown in Fig. 1, with a pressure difference $p' - p''$. In practice p'' was made zero by the application of a cold bath to B. Knudsen's results obtained by this method are about one half as large as those of Morley, and also of van der Plaats, in the region 0 to 40° C. The fact that mercury requires an appreciable time for evaporation might tend to produce such an effect since p' at the opening is being relieved continuously.

[1] Phil. Mag., Vol. –, p. 662, 1904.

[2] Ann. der Physik. 28, p. 75, 1908–9; ibid., 28, p. 999, 1908–9; ibid., 29, p. 179, 1909.

EXPERIMENTAL.

From the foregoing it seems desirable that there should be additional experimental data taken at ordinary working temperatures. The Knudsen pressure gauge, in the opinion of the writer, offered the most dependable method for such measurements since in its action it is independent of the nature of the gas, and also its range is approximately that of the vapor pressures to be measured. The Knudsen gauge available was not arranged to be used as an absolute manometer, but was calibrated by means of an accurately constructed McLeod gauge. The principle upon which the Knudsen[1] gauge depends is that the molecules of a residual gas in a partial vacuum are thrown off from a heated platinum foil, and striking a light and suitably suspended vane exert a couple, thus producing a deflection which may be read by means of an optical system. The deflection for zero pressure of course is zero. This fact makes it possible to use a McLeod gauge for calibration purposes, since calibration curves may be used with the origin as an accurately determined point. The McLeod gauge may be read quite accurately to .001 mm., or even less, provided the glass and mercury are kept clean.

A special pyrex glass McLeod gauge was constructed for the purpose and fused directly to the rest of the apparatus (including the Knudsen gauge) which was also of pyrex glass. The volume tube of the McLeod gauge was made comparatively large in order to lessen friction and surface-tension effects. The gauge was found to read consistently to .0005 mm. if the mercury and glass were kept clean. The apparatus was assembled as shown in Fig. 2. The Knudsen gauge *A*, and the sample

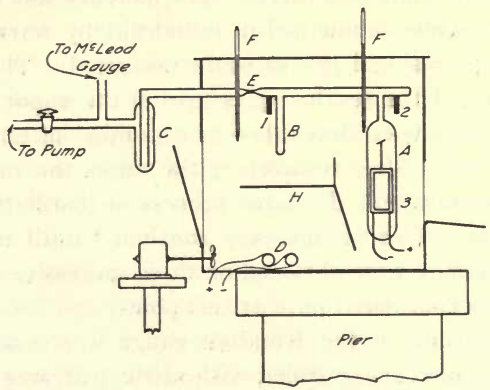

Fig. 2.

container *B*, were rigidly supported within a tight asbestos lined wooden box. The apparatus within the box was connected to the pumping

[1] Ann. der Physik, 32, pp. 809–842, 1910; PHYS. REV., 12, pp. 70–80, 1918.

system and McLeod gauge without through a tube of rather large diameter and including a mercury trap *C*. The system was evacuated by means of a Langmuir condensation pump supported by a Gaede rotary mercury pump. By continued pumping and with liquid air surrounding the trap *C* the pressure was readily brought down to about .005 mm. Hg. It was then further reduced by approximately equal steps. At each step the pressure as indicated by the McLeod gauge was accurately read simultaneously with the deflection of the Knudsen gauge, while a given constant current flowed through the platinum foil of the gauge. In this way data for a calibration curve were obtained. To test the consistency of the readings (for both gauges) sets of data were taken in which the current supplied to the gauge had in turn the values .3, .4, .5, .6 ampere. This data when plotted on 40 cm. coördinate paper gave, for each set, a smooth curve, showing that the two gauges were at least consistent.

The sample of mercury was then introduced into the container *B* and with liquid air surrounding the trap *C*, and the pumps running, the mercury was distilled slowly out of the container *B* and back again by heating first the container and then the rest of the tube. This process of distillation was carried out a number of times. Warm water was kept on the sample to prevent loss of the sample and condensation of vapors while the entire tube within the asbestos-lined box was heated to a temperature of 250 to 300° C. for several hours in order to drive the vapors out of the walls of the tube. The apparatus was then sealed off at *E*. After allowing the box to come to the desired temperature for a time, the total pressure was taken. The mercury was then driven into the container *B*, while submerged in liquid air, by warming the rest of the tube, and the residual gas pressure measured. The difference between the total and the residual pressures is the vapor pressure of the mercury. Readings were thus taken at a number of temperatures over the range 0 to 35°. After completing the series the tube was opened, resealed to the pump and the same process of distillation and heating carried out again. This method was continued until minimum values for the vapor pressure were obtained on three successive sets of readings. The mercury was considered pure at this point.

Another calibration of the Knudsen gauge was now carried out, a second sample of mercury, purified with nitric acid, was introduced and the process of distillation and heating was repeated eight times. The tube was then sealed off again at *E* and readings were taken at several different temperatures.

The four sets of data obtained in this way contained nineteen indi-

vidual values for the vapor pressure of mercury extending over the temperature interval of $-.7$ to $34.9°$ Centigrade. Of these values two or three differ from the mean curve by about 6 per cent., the rest being within 3 per cent. of the curve. In the following discussion it will be shown that this is about the accuracy that could be expected from the method.

The temperatures within the asbestos-lined box were read by means of two tenth-degree mercurial thermometers placed at different points. To insure uniform temperature the air was caused to circulate within the box by a fan driven by a motor without. The fan system was supported separately from the pier and box to prevent jarring the Knudsen gauge. The circulation of the air was directed by the bafflers *H*. Two heating coils, *D*, controlled the high temperatures, while the low temperatures were obtained by opening the windows and cooling the room. In general the temperatures were held constant, probably at .1 or very readily at .2° C. Changes of .2° in the box temperature produced changes in the vapor pressure that were just detectable by the Knudsen gauge. The gauge did not register changes as quickly as the thermometers. The Knudsen gauge was read by a lamp and scale at one meter distance. In order to hold the zero point, or rather to hold the vane and foil at a constant distance, the scale was rigidly fixed to the floor. If the vane became displaced, it could be brought back to its original position by merely restoring the zero on the scale. One set of calibration curves was used for three sets of data, and between each set the calibration was checked to make sure that it remained constant.

In order to determine the probable accuracy of the method some of the sources of error and their probable magnitude will now be considered. In the first place, impurities tend to increase the vapor pressure in the tube, so that this method would be expected to give values too high. The first sample gave minimum values for about eight distillations, and since the process of distillation was carried out more than twenty times, this error was considered eliminated. The second sample was first treated with nitric acid and then distilled eight times, hence we were justified in considering that the errors due to impurities in this sample were negligible. Special care was taken to keep the McLeod gauge and the mercury in it clean in order to prevent changes in friction. It was found that upon taking several readings at the same pressure the gauge could be read to within a total range of $\pm$ 2 per cent., except at the low pressures and these seemed to check well with the other readings as shown by the curves. The accurately known point on the curve at the origin helped to take care of this source of error. There was a

variation of 3 per cent. in the Knudsen gauge readings, however, if a new set of calibration curves were drawn through the same points, a variation would be obtained that would account for most of this error. Allowing for a probable error of ± 2 per cent. for temperature variations and the same for each of the other sources of error, the total probable error should be within about ± 6 per cent. The fact that this is the range of the actual readings seems to indicate that the principle sources of error have been accounted for and the data are about what one should expect from the method.

TABLE II.

Third Run of Data.

I.	R_0.	*R.*	Deflection.	Total Pressure from Curve.	Mean.	Temperature.
.3	9.8	13.0	3.2	.00277		
.4		15.3	5.5	.00274		25°
.5		18.0	8.2	.00276		
.6		20.9	11.1	.00272	.00275	
.3	10.0	14.32	4.32	.00432		
.4		17.3	7.3	.00438		30.8
.5		20.7	10.7	.00422		
.6		24.5	14.5	.00416	.00427	
.3	10.0	15.0	5.0	.0055		
.4		18.55	8.55	.00556		34.3
.5		22.5	12.5	.0054		
.6		26.75	16.75	.00514	.00540	
.3	9.7	11.05	1.35	.00087		
.4		12.02	2.32	.00088		
.5		13.19	3.49	.00089		11.6
.6		14.5	4.8	.00088	.00088	
.3	10.2	10.8	.6	.00033		
.4		11.17	.97	.00036		−.7
.5		11.7	1.5	.00036		
.6		12.35	2.15	.00036	.00035	
				Residual Pressure from Curve.		
.3	10.15	deflection hardly perceptible				
.4		10.19	.04	.00002		
.5		10.23	.08	.00002		
.6		10.28	.13	.00002	.00002	

One set of the actual readings taken is given in Table II. which constituted the third run in the first series. The total pressure for a given

temperature is given in the fifth column for different values of current flowing through the Knudsen gauge. The mean of these is recorded in the sixth column. At the bottom of the table is the data giving the residual gas pressure. Obviously the total pressure less this gas pressure is the vapor pressure of mercury. Table II. contains the data for the vapor pressure of mercury at five different temperatures. A second series, in which a new sample of mercury cleaned with nitric acid as noted earlier, gave values of the vapor pressure for additional temperatures. Together the two series gave nineteen values extending over a range in temperature from $-.7$ to 34.9° C. which are collected in Table III. The corresponding graph is shown in Fig. 3. The points

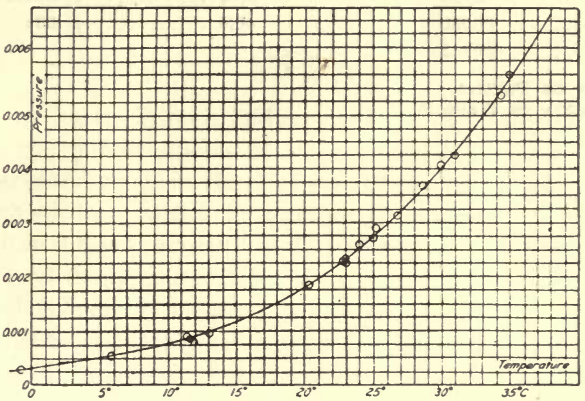

Fig. 3.

TABLE III.

Values for the Vapor Pressure of Mercury at Various Temperatures.

Temperature.	Pressure mm. Mercury.	Temperature.	Pressure mm. Mercury.
−.7°	.00033	24.0°	.00262
5.7	.00055	25.0	.00273
11.4	.00092	25.6	.00292
11.6	.00086	26.8	.003145
11.6	.000815	28.6	.0037
13.0	.00097	29.9	.004075
20.3	.00187	30.8	.00425
22.8	.00230	34.3	.00538
23.0	.00224	34.9	.00575
23.0	.00235		

all lie well upon a smooth curve. In Table IV. the vapor pressure of mercury in mm. is given for 2-degree intervals taken from the curve.

In conclusion, the author wishes to thank Professor A. P. Carman for the use of the facilities of the laboratory, and also to thank Professor

C. T. Knipp for the interest he has taken in the work and for the many suggestions offered.

TABLE IV.

Values for Each 2° as Taken from Smooth Curve Through the Points.

0.0°	.000350 mm. Hg.	22.0°	.00214 mm. Hg.
2.0	.000412	24.0	.00234
4.0	.000487	26.0	.003
6.0	.000572	28.0	.0035
8.0	.000662	30.0	.00407
10.0	.000775	32.0	.00467
12.0	.000895	34.0	.00535
14.0	.00105	36.0	.00607
16.0	.00126	38.0	.00695
18.0	.00150	40.0	.008
20.0	.00182		

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VITA

Charles Francis Hill received his early education in the public schools of Illinois, and his college preparatory work in the Eastern Illinois State Normal School from which he graduated in 1911. He then entered the University of Illinois, from which he received the degree of A.B., in 1914. From 1914 to 1921 he has been an assistant in physics at the University of Illinois, doing part-time graduate work, having received the degree of A.M., in 1916.